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Article

A quarterthiophene based dye as an efficient interface modifier for Hybrid Titanium dioxide / Poly(3-hexylthiophene)(P3HT) Solar Cells

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Abstract: This work focuses on studying the influence of dyes, including a 3-hexylthiophene derivative dye with a cyanoacrylic acid group ((E)-2-cyano-3-(3',3'',3'''-triethyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-yl) acrylic acid)(4T), on the photovoltaic performance of titanium dioxide (TiO₂) / poly(3-hexyl thiophene)(P3HT) solar cells. The insertion of dye at the interface improves the efficiency regardless of the dye used. However, 4T dye significantly improves the efficiency by a factor of three when compared to the corresponding control. This improvement is mainly due to increase in short circuit current density (J_{sc}), which is consistent with higher hole-mobility reported in TiO₂ / P3HT nanocomposite with 4T dye. Optical absorption data further reveals that 4T extends the spectral response of the TiO₂ / P3HT nanocomposite which could also enhance the J_{sc}. The reduced dark current upon dye insertion ensures that the carrier recombination is controlled at the interface and this in turn increased the open circuit voltage. Optimized hybrid TiO₂ / P3HT device with 4T dye as an interface modifier showed average efficiency over 2 % under simulated irradiation of 100 mWcm⁻² (1 sun) with Air Mass 1.5 filter.

Keywords: Hybrid solar cells, Titanium dioxide, Poly(3-hexylthiophene), oligothiophene dye, interface modifier, photovoltaic, absorption, quantum efficiency, polymers, efficiency

1. Introduction

Hybrid nanoporous metal oxide – polymer photovoltaic devices have intensively been studied for more than two decades as these offer the potential advantages relative to organic acceptors of low cost, facile synthesis via wet chemical processing, control of heterojunction morphology, and the potential for higher physical and chemical stabilities [1]. A metal oxide nanoparticle (TiO₂, ZnO) percolation network with thickness in the submicron scale provides the stable and transparent backbone network for free carrier transport in this type of solar cells [2]. However, the power conversion efficiency (PCE) of these hybrid devices is limited due to several reasons including interfacial carrier recombination [3,4] at the interface, poor mobilities in metal oxide / polymer nanocomposite and poor spectral response of polymer [5–8]. Typically, the nanoporous metal oxides are the electron acceptors and the π -conjugated polymers are the donors [9–11] in hybrid metal oxide / polymer solar cells. The electron transfer from a donor into an acceptor produces a large proportion of charge carrier pairs across the donor / acceptor interface. In that situation, the Coulombic attraction

of these bound charge carrier pairs limit the device performance by feeding the recombination effects at the interface [8,12–14]. It has been shown that engineering the metal oxide – polymer interface can improve the PCE of hybrid solar cells [12,15–17]. Using nanolayers of absorber materials could improve the spectral response and reduce the interfacial recombination [18,19]. Organic dye molecules were also widely investigated as the interface modifier for metal oxide / polymer solar cells. In addition to number of natural dyes[20–24], N719 and Z907 are two of the most common Ruthenium based dyes which are successfully used as an absorber material in highly efficient dye sensitized solar cells [25,26]. These dyes were also efficiently used as an interface modifier in solid state hybrid solar cells and are found to improve the spectral response by participating in carrier generation, limiting the recombination [27] at the interface and hence improving both short circuit current density (J_{sc}) and the open circuit voltage (V_{oc}).

Planells M. *et al.*, reported a series of 3-hexylthiophene derivative dyes with a cyanoacrylic acid group with conjugation length from one to five thiophene units (1T to 5T) as interface modifiers at TiO_2 / P3HT solar cells [16]. These dyes are metal ion free dyes and have an electron rich thiophene group. It was found that the dyes improve the V_{oc} due to a dipole moment at the interface [16,28]. Oligothiophenes are discrete, monodisperse molecules and are distinct from polythiophene which inherently exists as a distribution of molecular weights. A pure carboxylated oligothiophene can be isolated from any unfunctionalized oligomers via column chromatography and recrystallization [28]. Such organic semiconducting oligothiophenes have been intensively investigated and widely used in organic photovoltaic (OPVs) due to the presence of excellent charge transport properties and tunable optical/electrochemical properties [29]. These tunable electrochemical properties successfully investigated with variation of thiophene unit, show energy gap reduction when increasing the number of thiophene units from 1T to 5T [16,30].

It has been reported that 4T dye at the interface was found to increase the hole-mobility in TiO_2 / P3HT polymer nanocomposite by a magnitude of ten times higher hole-mobility compared to the corresponding untreated nanocomposite. This is due to passivation of surface traps by the dye as well as improved packing of the polymer with the nanocrystals through effective inter-chain interactions of 4T with P3HT [8]. The molar extinction coefficient (MEC) is an important parameter in defining the amount of material to be loaded on an electrode for maximum energy conversion particularly at thin layers of acceptors. It is also reported that the dyes with higher MEC can improve the stability of dye based solar cells [31]. Given that the 4T dye can improve the performance of TiO_2 -P3HT solar cells by involvement in photocurrent generation, the amount of dye molecule at the interface needs to be optimized. It was found that the MEC of 4T dye is higher than that of N719 and Z907 dyes. This work enhances the performance of hybrid TiO_2 / P3HT polymer solar cells by optimizing the device fabrication conditions with dyes and investigates the role of 4T dye at the metal oxide – polymer interface in enhancing the performance of hybrid TiO_2 / P3HT polymer solar cells.

2. Materials and Methods

Solar cell fabrication: The solar cells were made using Indium Tin Oxide (ITO) coated glass substrates (12 mm × 12 mm, 10 Ω / square). All the chemicals and solvents used in this work were purchased from Sigma Aldrich. The cleaned ITO substrates were first spray coated with a diluted solution of titanium (iv) isopropoxide and acetylacetone mixture [8] in ethanol at a substrate temperature of 500 °C and, baked at the same temperature for 30 minutes in order to form ~50 nm thick dense/blocking TiO_2 layer. Thereafter, a mesoporous TiO_2 layer was spin coated on top of the dense TiO_2 with the solution (240 mg ml⁻¹) of TiO_2 paste (18NRT) (Dyesol, Australia) [30,32,33] dissolved in tetrahydrofuran [8] and allowed to sinter at 450 °C for 30 minutes [34]. As in previous studies [8,11,35], we have used 0.3 mM concentrated dyes Z907 (M_w = 870.10), N719 (M_w = 1188.55) and 4T (M_w = 678.05) by dip coating for 16 hours at 90 °C in order to modify the mesoporous TiO_2 films. The chemical structures of the dyes and polymer used in this work are shown in figure 1.

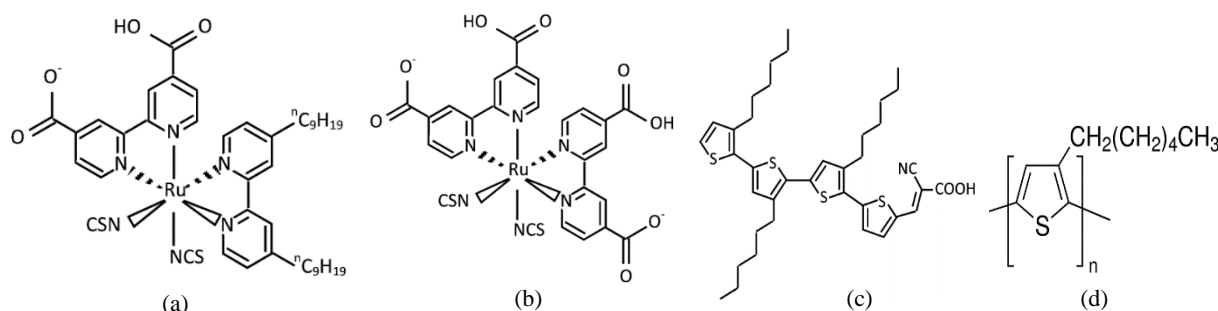


Figure 1. Chemical structure of dyes and polymer used: (a). Z907 [8], (b). N719 [8], (c). 4T [8,16] and (d) P3HT.

The influence of concentration of interface modifier on the device performance was examined with various concentrations of 4T dye. In each situation, the dye solutions were prepared using a 1:1 volume ratio solvent mixture of acetonitrile with tert-butanol [8,30,32]. After dye dipping, the electrodes were washed in 1:1 volume ratio mixture of acetonitrile with tert-butanol to remove excess dye in the nanoporous layer [8]. The dye modified electrodes were first dip coated with 2.5 mg ml⁻¹ P3HT (Merck KGaA, Germany) and then spin coated with (25 mg ml⁻¹) P3HT solution dissolved in chlorobenzene, and 100 nm of Gold top contact by thermally evaporation under high vacuum was deposited as described in refs [3,18,19] through Edwards E306 thermal evaporator. On dye modified electrodes with dip (2.5 mg ml⁻¹), P3HT (25 mg ml⁻¹) from Merck KGaA, Germany solution dissolved in chlorobenzene was spin-coated, and the solar cells were fabricated by depositing 100 nm of Gold top contact by thermally evaporating under high vacuum as described in refs [3,18,19] through Edwards E306 thermal evaporator. Finally, the fabricated solar cell devices were allowed to anneal process with nitrogen medium at 120 °C for 10 min in order to improve the interfacial characteristics [36].

Optical Characterization: UV-Vis. measurement of the dye coated TiO₂ films were recorded by using a JENWAY 6800 UV/Vis. Spectrophotometer, which was controlled using Flight Deck software. The thickness of TiO₂ and P3HT layers recorded by Field Emission Scanning Electron Microscopy (FESEM, ZEISS Sigma, UK)

Electrical characterization: The electrical characterization of both polymer and solid state solar cells were tested, and the current-voltage curves recorded with a computer controlled Keithley 2400 source meter unit under the conditions of dark and 100 mW/cm² illuminations of the solar simulator (SCIENCE TECH, Canada) with AM (Air Mass) 1.5 spectral filter. The External quantum efficiency (EQE) measurements were carried out with a Monochromator (Newport, USA) and a calibrated silicon photodiode (Newport, USA).

3. Results

Figure 2 (a), (b) and (c) compares optical absorption spectra of dyes (4T, N719 and Z907) dissolved in tert-butanol and acetonitrile solution with 0.3 mM concentration, dye dip coated nanoporous TiO₂ electrodes and dye, polymer dip coated nanoporous TiO₂ electrodes. It is clear that peak Molar Extinction Coefficient (MEC) of 4T dye is a factor of two higher than the other two standard dyes. P3HT has broader absorption spectrum in the visible region when compared to the metal-complex dyes and the absorption spectrum of the 4T dye compliments the polymer absorption in the visible region. Figure 2 further shows that the polymer uptake and visible light absorption of the electrode treated with 4T dye is much higher than the electrodes treated with N719 and Z907 dyes. This is probably due to higher MEC of 4T and better compatibility between thiophene based dye and poly(3-hexyl thiophene). Combining of thiophene units of 4T with poly(3-hexyl thiophene) increases the overall thiophene units in the π -conjugated system, which leads in the red shifted and broadened absorbance spectrum under UV/Visible region [37].

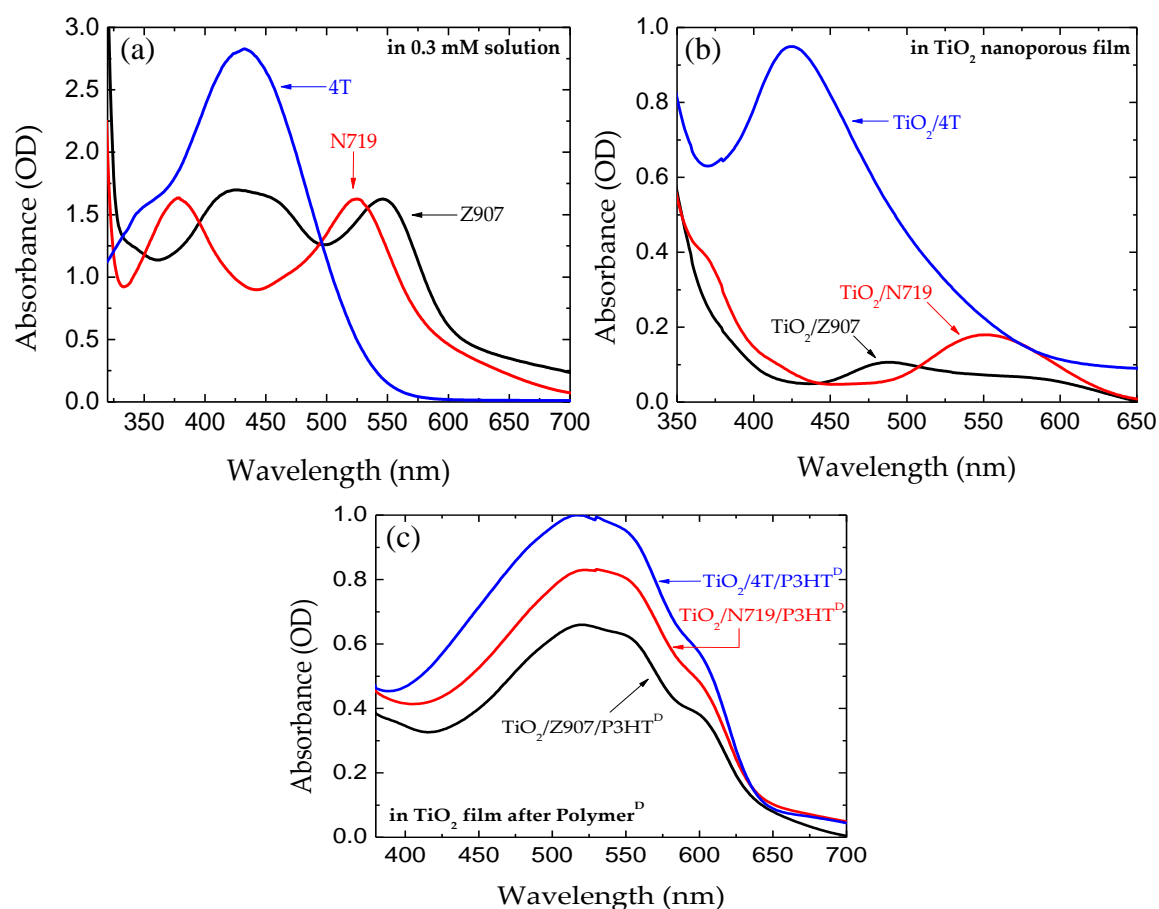


Figure 2. Optical absorption spectra of (a) 0.3 mM concentration of dyes dissolved in tert-butanol and acetonitrile solution, (b) dye dip coated nanoporous TiO₂ electrodes and (c) dye, polymer dip coated nanoporous TiO₂ electrodes

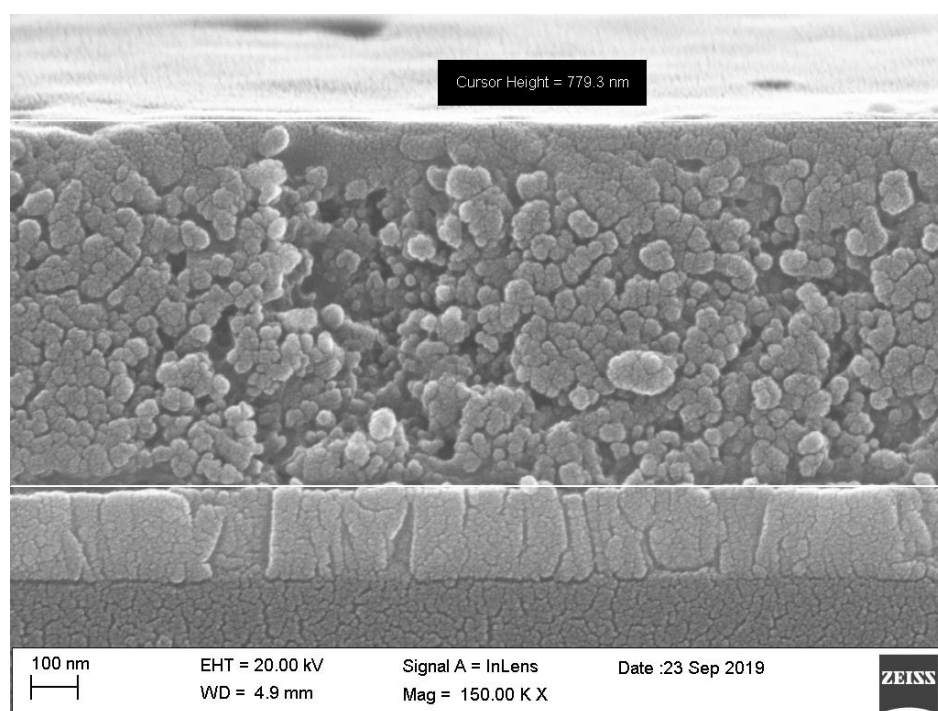


Figure 3. Cross sectional Field Emission Scanning Electron Microscopy (FESEM) image for fabricated TiO₂ / 4T / P3HT solar cell.

To confirm the dimensions of the layer we performed FESEM on the samples. A completed device is cut into two and the cross section of the device was examined. The cross sectional FESEM image of the completed device is shown in Figure 3. It clearly shows that thickness of the TiO₂/4T/P3HT nanocomposite is about 780 nm in which about 150 nm excess polymer layer which could serve as an electron blocking layer (block direct contact between TiO₂ nanoparticles and top contact). (For FESEM images of each layer, please refer to the figures SM1 to SM4 in appendix).

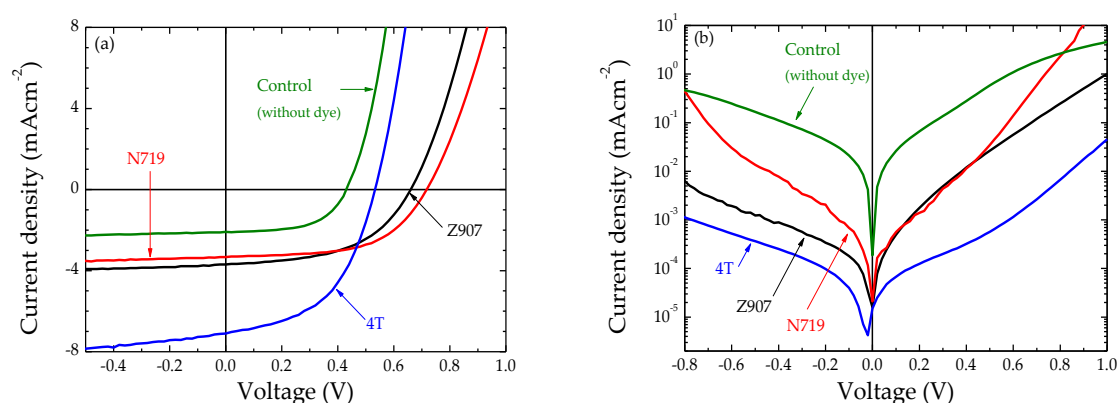


Figure 4. (a) J-V characteristics of the fabricated TiO₂/P3HT and dye modified TiO₂/P3HT solar cells under simulated irradiation of 100 mWcm⁻² (1 sun) with Air Mass 1.5 filter and (b) semi-log J-V plot of the solar cells in dark. The complete structure of control device is ITO/TiO₂/P3HT/Au, and the dye modified cells have the structure ITO/TiO₂/dye/P3HT/Au. Here dyes Z907, N719 and 4T are used as the interface modifiers.

Table 1. Current density vs. voltage measurement data for control device and other corresponding dye modified devices

Condition	$J_{sc}(mAcm^{-2})$	$V_{oc}(V)$	FF%	Efficiency %
Without dye (control)	2.09	0.44	44	0.41
N719	3.33	0.65	39	0.86
Z907	3.70	0.71	38	1.01
4T	7.30	0.57	49	2.04

Figure 4 (a) and table 1 clearly show that the insertion of dye molecules at the TiO₂/P3HT interface increases the short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and subsequently the PCE. However, the devices with 4T dye treated electrodes showed maximum efficiency of about 2 % which is five-fold higher than that of the corresponding control TiO₂/P3HT devices without any dye treatment. This is mainly due to a fourfold increment in the J_{sc} . This can be attributed to increased hole-mobility of P3HT due to the insertion of 4T dye [8] at the interface between TiO₂/polymer interface. Figure 4 (b) shows that the dark current was significantly suppressed in dye treated devices in comparison with corresponding control. This is an indication of reduced back electron transfer [38]. The lowest dark current was observed in 4T dye treated devices which is three order of magnitude lower than that of the corresponding control device. This may suggest that the metal complex dyes have a more beneficial effect in shifting up the TiO₂ conduction band energy. Then the external quantum efficiency (EQE) spectra of the dye treated and untreated TiO₂/P3HT devices were measured. Figure 5 illustrates the EQE spectra of all devices tested. The conversion efficiency in polymer increased regardless of the dyes used. Figure 5 clearly shows that the influence of dyes N719 and Z907 carrier generations are minimal in the fabricated devices, while influence of 4T dye on carrier generation is dominant with peak external quantum efficiency over 60 % at peak absorption

of 4T dye. This is probably attributed to improved hole-mobility caused by the 4T dye and better compatibility of the oligothiophene dye with poly(3-hexyl thiophene) polymer.

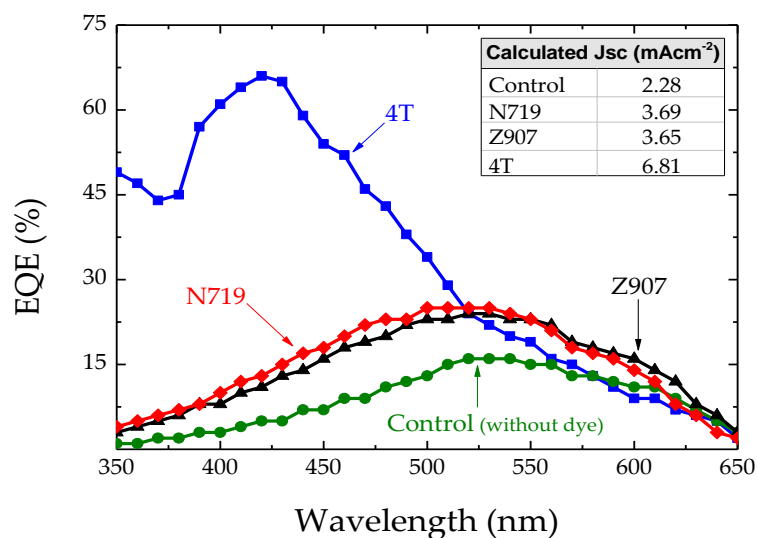


Figure 5. External Quantum Efficiency of ITO/TiO₂/P3HT/Au (control) and ITO/TiO₂/dye/P3HT/Au (interface modified) solar cells. Here the dyes Z907, N719 and 4T are used as the interface modifiers in TiO₂/P3HT solar cells. Inset table presents the calculated J_{sc} from the EQE graph.

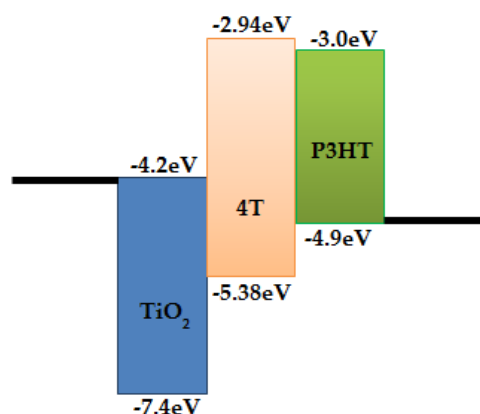


Figure 6. Schematic energy band diagram of the TiO₂/4T/P3HT solar cell

Further, figure 4 shows that dye treatment, especially 4T dye significantly suppresses the dark current and increases both open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) under simulated solar irradiation, relative to the case where the device without dye. This is consistent with schematic energy band diagram of the TiO₂ / 4T / P3HT device shown in the Figure 6 where deep HOMO level of 4T relative to P3HT, the 4T layer is expected to obstruct hole transfer between P3HT and TiO₂, and thus to localize hole-polarons in the P3HT away from the TiO₂ surface. Energy levels for TiO₂ [18], 4T [16] and P3HT [16,18,39] in figure 6 are directly taken from literature.

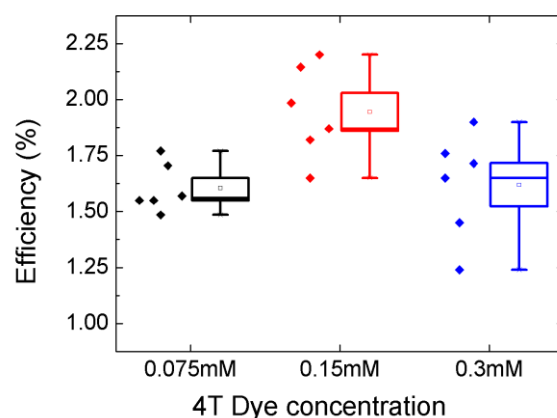


Figure 7. Distribution of power conversion efficiencies of 6 cells fabricated with three different concentrations. (Box indicates the standard deviations, whiskers indicate the range, and the small square in the middle of each box indicates the average)

As in Figure 3(a), the extinction coefficient of the 4T dye is higher than that of N719 and Z907 dyes. To find the optimum dye concentration for maximum energy conversions, TiO₂ electrodes with different concentrations of 4T dye were studied. Figure 7 summarizes the variation of PCEs of 6 cells fabricated with three different concentrations of 4T dye. The average power conversion efficiency was maximum at 0.15 mM with a champion efficiency over 2.0 %. Table 2 compares the PCEs of solar cells in this work with recently reported TiO₂ / P3HT solar cells with various interface modifiers including dyes. The table clearly shows that the 4T dye modified devices showed the best PCE of the device with pristine P3HT and nanoporous TiO₂ electrode. It should be noted that our devices have TiO₂ nanoparticles which did not undergo TiCl₄ treatment.

Table 2. PCEs of recently reported TiO₂ / P3HT solar cells with various interface modifiers including dyes.

Device structure - different interface modifiers	Efficiency %	Year	Reference
TiO ₂ / carboxylated oligothiophene / P3HT	0.11	2015	[28]
TiO ₂ / BT5 oligomer / P3HT	0.21	2019	[10]
TiCl ₄ treatment / TiO ₂ nanorod / ACA /P3HT	0.28	2015	[40]
TiO ₂ / TiCl ₄ treatment / [6,6]-Phenyl C61 butyric acid / P3HT	0.37	2015	[41]
TiO ₂ / TiCl ₄ treatment / D131 / P3HT	1.53	2015	[41]
TiO ₂ / TiCl ₄ treatment / squaraine dye SQ2 / P3HT	2.22	2015	[41]
TiO ₂ nanorod / P3HT / PEDOT:PSS	0.43	2012	[15]
TiO ₂ nanorod(650 nm) / D149 / P3HT / PEDOT:PSS	1.58	2012	[15]
TiO ₂ nanorod(1.5 μm) / D149 / P3HT/ PEDOT:PSS	3.12	2012	[15]
TiO ₂ nanorod / Z907 / P3HT / PEDOT:PSS	0.94	2012	[15]
TiO ₂ nanowires / Pyridine / P3HT	0.45	2015	[42]
TiO ₂ / Z907 / P3HT / PEDOT:PSS	0.53	2017	[35]
TiO ₂ nanowires / TiCl ₄ treatment / CdS /P3HT	0.7	2015	[42]
TiO ₂ nanofibers / N719 / P3HT	0.90	2010	[43]
TiO ₂ / Nitro Benzoic Acid treatment / P3HT / PEDOT:PSS	1.05	2017	[3]
TiO ₂ nanofibers / N719 + PPA / P3HT	1.09	2010	[43]
TiO ₂ / Methoxy Benzoic Acid treatment / P3HT/ PEDOT:PSS	1.24	2017	[3]
TiO ₂ / Al ₂ O ₃ / N719 / P3HT / PEDOT:PSS	1.4	2014	[38]
TiO ₂ / TiCl ₄ treatment / 4T / doped P3HT	1.54	2014	[16]
TiO ₂ / TiCl ₄ treatment / 5T / doped P3HT	2.32	2014	[16]
TiO ₂ nanorod / TiCl ₄ treatment / D149 / TBP / P3HT / PEDOT:PSS	1.83	2012	[44]
TiO ₂ / triphenylamine dye / P3HT	2.01	2016	[45]
TiO ₂ / Z907 / P3HT	1.01	2019	Current work
TiO ₂ / N719 / P3HT	0.86	2019	Current work
TiO ₂ / 4T / P3HT	2.04	2019	Current work

4. Conclusions

Three different dyes including a metal free 4T dye as an interface modifier at TiO_2 / P3HT solar cells were investigated. It was found that the commercial dyes N719 and Z907 improve the performance of the solar cells by improving the hole-mobility of the polymer and by reducing the back-electron transfer at the interface. Among all the dyes used, the insertion of 4T dye improved the efficiency by fivefold which is higher when compare to other dyes used. Optimized nanoporous TiO_2 / P3HT solar cells with 4T dye yielded maximum efficiency over 2 % under 1 sun illumination with an AM 1.5 filter. This is attributed to a combination of charge carrier generation due to 4T dye, as shown by EQE spectra data, and improved morphology and mobility of the P3HT caused by the 4T.

Supplementary Materials:

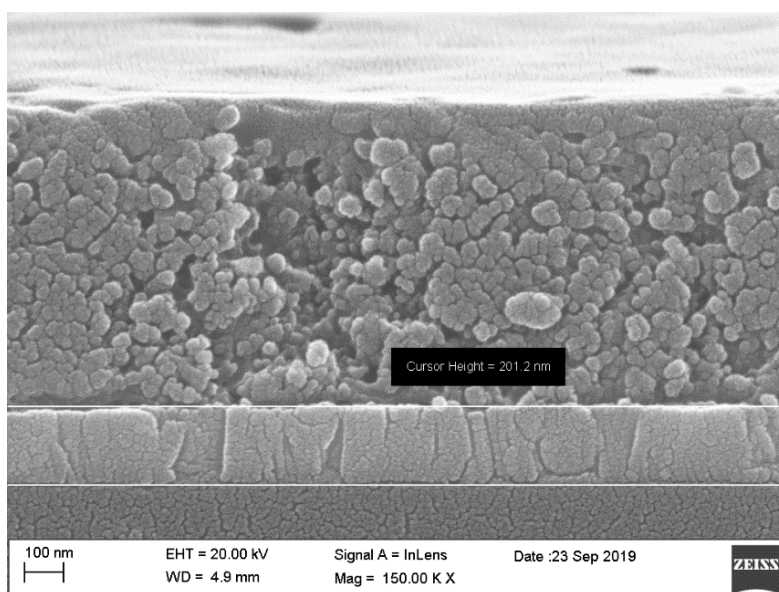


Figure SM1. Cross sectional FESEM image for fabricated TiO_2 / 4T / P3HT solar cell. The thickness of ITO layer was found to be 201.2 nm.

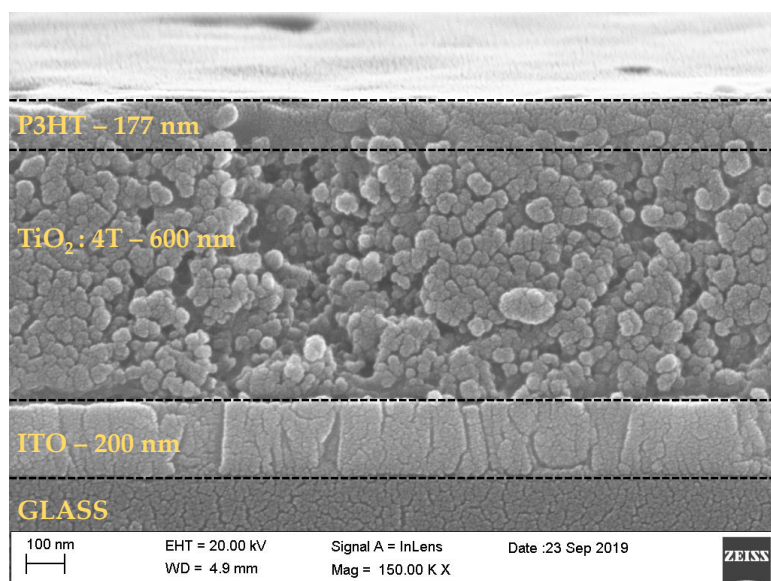


Figure SM2. Cross sectional FESEM image for fabricated TiO_2 / 4T / P3HT solar cell with individual thickness for each layer.

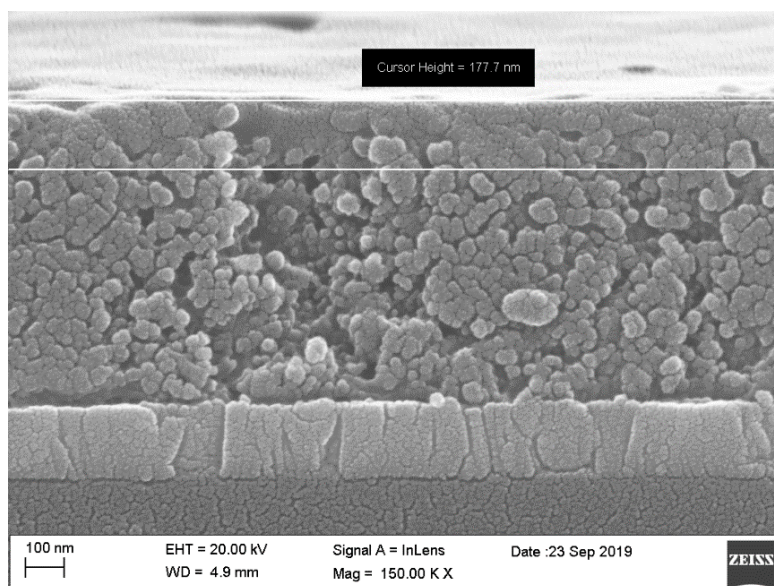


Figure SM3. Cross sectional FESEM image for fabricated TiO_2 / 4T / P3HT solar cell. The thickness of P3HT layer was found to be 177.7 nm.

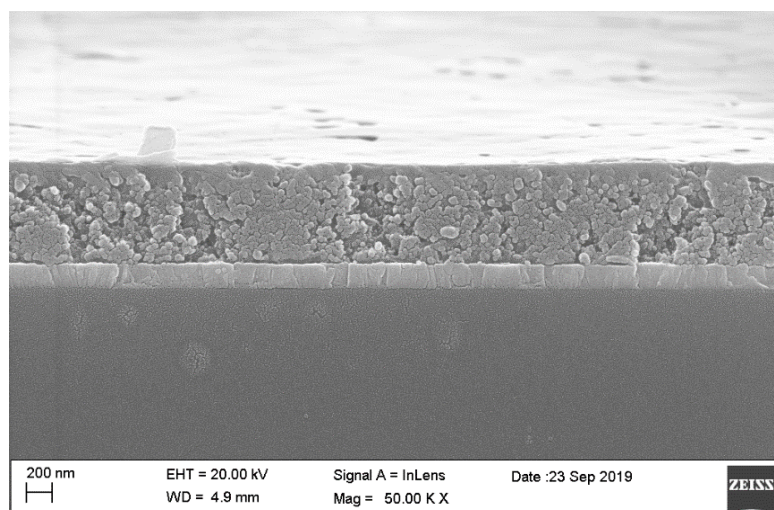


Figure SM4. Cross sectional FESEM image for fabricated TiO_2 / 4T / P3HT solar cell.

Author Contributions: Conceptualization, Pirashanthan Arumugam, Thanihaichelvan Murugathas, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Data curation, Pirashanthan Arumugam, Thanihaichelvan Murugathas, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Formal analysis, Pirashanthan Arumugam, Thanihaichelvan Murugathas, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Funding acquisition, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Investigation, Pirashanthan Arumugam, Thanihaichelvan Murugathas, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Methodology, Pirashanthan Arumugam and Thanihaichelvan Murugathas; Project administration, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Resources, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Software, Pirashanthan Arumugam and Thanihaichelvan Murugathas; Supervision, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Validation, Pirashanthan Arumugam, Thanihaichelvan Murugathas, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Visualization, Punniamoorthy Ravirajan and Dhayalan Velauthapillai; Writing – original draft, Pirashanthan Arumugam; Writing – review & editing, Thanihaichelvan Murugathas, Neil Robertson, Punniamoorthy Ravirajan and Dhayalan Velauthapillai.

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Conflicts of Interest: The authors declare no conflict of interest

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